



CO₂ photoreduction at high pressure to both gas and liquid products over titanium dioxide



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ABSTRACT

The photoreduction of CO₂ is an intriguing process, which allows the synthesis of fuels and chemicals. Several semiconductors were prosed during the last years in order to overcome the limitations of light harvesting and limit electron-hole recombination. Unfortunately, the reaction mechanism and the investigation of alternative photo-reactors are still insufficiently investigated, leading to a limited efficiency of the whole process. In this work, a deep study was carried out by means of an innovative photo-reactor operating under high pressure, with the aim to shed light on the complex reaction pathways towards both liquid and gas phase photoreduction products. Products distribution was compared after different reaction time in batch mode. Formaldehyde was the major product at the beginning of the reaction, followed by formic acid. The previously suggested hypothesis of consecutive formation of the acid and subsequently of formaldehyde through further reduction is here replaced by a parallel reaction scheme, especially valid when working in basic conditions. Furthermore, gas phase products, mainly constituted by H₂ and CO, start forming and accumulating only after the consumption of the inorganic hole scavenger. Therefore, their synthesis is ascribed to photoreforming of the organic products, which are the main CO₂ photoreduction products. Such organic species may act as alternative hole scavengers. Productivity as high as 102 mmol h⁻¹ kg_{cat}⁻¹ for H₂, 16537 mmol h⁻¹ kg_{cat}⁻¹ for formaldehyde and 2954.37 mmol h⁻¹ kg_{cat}⁻¹ for formic acid were achieved when operating at a 7 bar of CO₂ over the aqueous solution, 80 °C with 0.5 g L⁻¹ TiO₂ by tuning reaction time and pH.

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1. Introduction

The continuous increase in CO₂ emissions, which is considered a harmful greenhouse gas generated by human and natural activities [1], is leading to a global warming that is dangerous for all living beings. CO₂ is a very stable compound and therefore recalcitrant to conversion into less harmful compounds. However, different studies were developed to find conditions for activating CO₂ and converting it into useful chemicals. Among them, the most interesting ones concern the conversion of CO₂ into other molecules, both chemically, for example formic acid [2], or its valorization through other catalytic processes [3]. Alternatively, CO₂ can be converted photochemically [4].

Photocatalysis represents a useful and powerful tool for the reduction of CO₂ because, compared to energy intensive chemical processes, it may exploit solar energy. Moreover, using a semicon-

ductor and light, the activation of substantially inert molecules, i.e. water and CO₂, can be achieved at low temperature [5]. In this view, photocatalysis is a smart way for the sustainable reduction of CO₂ emissions in the presence of H₂O.

CO₂ could be converted into useful compounds such as carbon monoxide, methane, methanol, formaldehyde and formic acid. One of the most studied photocatalysts for this process is TiO₂ due to its resistance to photocorrosion and low cost [6]. However, the drawbacks of using TiO₂ as a catalyst are the large band gap and the fast recombination rate of holes and electrons generated during the irradiation process that lead to a reduction of the efficiency of the catalyst. To overcome this problem, various strategies have been developed including the addition of small amounts of noble metals (e.g. Au, Cu, Ag) [7,8], generally used as electron sinks, and/or the use of organic or inorganic hole scavengers, which reduce the phenomenon of recombination of the photogenerated charges. These compounds are reducing agents which donate electrons to the valance band of the semiconductor to prevent holes accumulation, which in turn favours their recombination with photopromoted electrons [9]. Although their usage enhance the rate of the process,

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their reaction produce a by-product, which has to be considered during their choice. The use of organic hole scavenger (especially alcohols) is deeply studied in literature [10]. However, in this work an inorganic hole scavenger was chosen as non-harmful compound without influence on the organic pool in liquid phase. Sodium sulfite was chosen thanks to its ability to be oxidized into sulfate by the photogenerated holes [11].

Paulino et al. tested a Cu-Zn promoted photocatalyst for this reaction, obtaining a productivity of methane of $7.66 \text{ mmol h}^{-1} \text{ kg}_{\text{cat}}^{-1}$ after 24 h of UV exposure [12]. Similarly, Mele et al. prepared composite materials based on polycrystalline TiO_2 and phthalocyanines or porphyrins and tested them for CO_2 reduction obtaining $28.62 \text{ mmol h}^{-1} \text{ kg}_{\text{cat}}^{-1}$ of formic acid as principal product [13]. Anpo et al. reported another example, in which TiO_2 was used to obtain CO and methanol as main products (7 and $4 \text{ mmol h}^{-1} \text{ kg}_{\text{cat}}^{-1}$, respectively) [14]. The mechanism of the reaction was studied by Izumi [6], and a consecutive reaction path first occurring in the liquid and then in the gas phase was proposed. Nevertheless, the investigation did not cover all the possible products of the process. All these investigations, together with others that could be found in literature, are useful for demonstrating two aspects: the first one is that the photoreduction of CO_2 is feasible but, on the other hand, that still some basic research, based on a rigorous approach should be carried out because at the moment productivity is very limited and there is not a deep comprehension of the photocatalytic process. Thus, the process is still very far from being optimised and one of the main limitations when operating in liquid phase is the poor CO_2 solubility in water.

We have already reported an innovative photoreactor concept, which would allow to improve CO_2 solubility in water at high pressure (up to 20 bar) [15,16]. This led to the successful production of both liquid phase (formic acid, formaldehyde) and gas phase (H_2 , CO, CH_4) products. The reaction paths leading to this complex spectrum of products are not trivially described. We preliminary hypothesized that H_2 would be produced by photoreforming of organic products forming in liquid phase during the first hours-on-stream, but evidences of this mechanism are still lacking.

Therefore, in this work, we have deepened the mechanism of the photoreduction of CO_2 in liquid phase (H_2O was used as solvent), using a commercial TiO_2 (Evonik P25) photocatalyst in the presence of Na_2SO_3 as hole scavenger and working at different pH. Particular attention was dedicated to the influence of operating parameters on the mechanism and kinetics of the reaction. Using the already described high-pressure photoreactor, we identified both liquid and gaseous products in variable amounts, depending on the reaction time and the operating parameters identified. Besides deepening the parametric dependence of H_2 and liquid organic products on operating variables, we also proposed a reaction pathway to explain products distribution.

2. Experimental

2.1. Photocatalysts and reactants

Commercial nanometric titanium dioxide P25 by Evonik was used as photocatalyst and suspended in water with a concentration of 0.5 g L^{-1} . It is a well-known mixture of anatase and rutile crystal phases whose morphology was deeply studied by Ohno et al. [17]. NaOH (Sigma Aldrich, 99%) was used to increase the pH to 14 (11.0 g L^{-1}).

Na_2SO_3 (Sigma Aldrich, 98%) was used as hole scavenger, with a concentration of 1.7 g L^{-1} . All these products were used without further purifications. The gas phase was analyzed by gas chromatography (Agilent, mod. 7890) equipped with a TCD detector and a proper set up for the quantification of H_2 , CH_4 , CO and

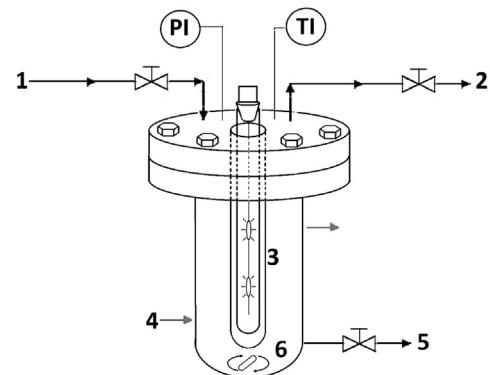


Fig. 1. Sketch of the high pressure photoreactor. 1: Pressure reducer, 2: Sample valve for gas phase, 3: Lamp, 4: Double-walled thermostatic system, 5: Sample valve for liquid phase, 6: Magnetic Stirrer. PI: pressure indicator; TI: temperature indicator.

Table 1

Summary of the tests performed.

Test	Time [h]	pH	Catalyst Mass [g]
1	70	14	0.6
2	24	14	0.6
3	16	14	0.6
4	6	14	0.6
5	3	14	0.6
6	24	14	0.3
7	24	7	0.6

polar/non polar light gases. Liquid phase was analyzed by HPLC (Agilent, 1220 Infinity) using a column (Alltech, OA-10308) with UV and refractive index (Agilent, 1260 Infinity) detectors. Aqueous H_3PO_4 solution (0.1 wt.%) was used as the eluent. The consumption of Na_2SO_3 was evaluated by iodometric titration. This method is based on the oxidation of sulphites (SO_3^{2-}) into sulphates (SO_4^{2-}) by iodine produced from a solution with a known concentration of potassium iodate (KIO_3 , Sigma Aldrich, 98%) and potassium iodide (KI , Sigma Aldrich, 99%) in acid environment and the subsequent titration of the iodine excess with sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$, Sigma Aldrich, 98%), the end point of the titration is detected using a starch solution as an indicator.

2.2. Photoreactor setup

Photocatalytic reduction of CO_2 with H_2O was carried out at a constant pressure of 7 bar and at a constant temperature of 80°C . A scheme of the experimental setup is reported in Fig. 1 [15,16]. It is an innovative pressurized batch photo reactor. It allowed operating pressure up to 20 bar of CO_2 , regulated by a pressure reducer (Fig. 1). The reactor is made of AISI 316 stainless with an internal capacity of 1.7 L; it is completed by a magnetic stirrer (400 rpm kept constant) ensuring a proper liquid mixing and the temperature is kept constant through a double-walled thermostatic system. As source of radiation, we used a 125 W medium-pressure Hg vapour lamp with a range of emission wavelengths from 254 nm to 364 nm, which was introduced vertically in the reactor axis. The emitted power was periodically measured by means of a photoradiometer (Delta OHM HD2102,2) and corresponds to 104.2 W m^{-2} at the bottom of the quartz candle. A pressure transducer and a thermocouple measured the pressure and the temperature inside the reactor respectively. At the end of each test, liquid and gas phase were sampled operating proper valves. A 27 cm long quartz candle, transparent to the UV radiation, was used to protect the lamp from the pressure. The harmful overheating of the lamp bulb was avoided by continuous heat removal by an air circulation system around the bulb, which also helped keeping the temperature of the solu-

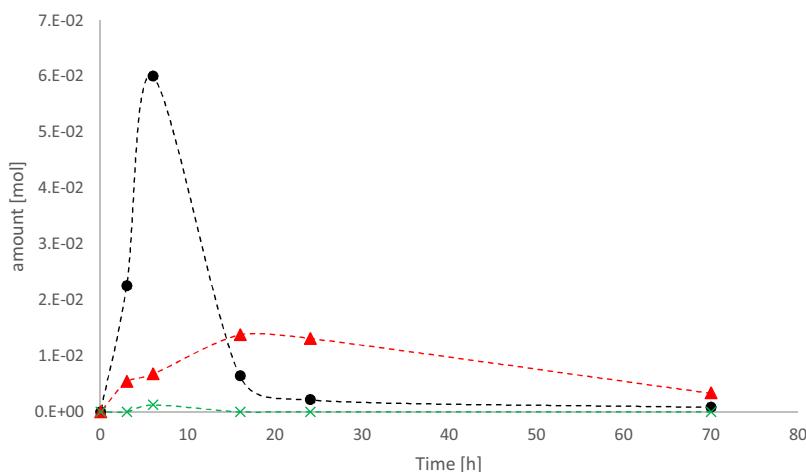
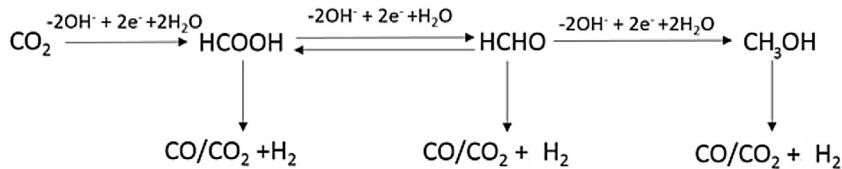


Fig. 2. Amount of liquid phase products, i.e. formic acid (▲), Formaldehyde (●) and Methanol (×), obtained in tests 1–5.



Scheme 1. Consecutive pathway for CO_2 photoreduction.

tion constant within $\pm 0.5^\circ\text{C}$. The thermocouple was in the central part of the quartz candle at a distance of 1 cm.

The photoreactor was filled with 1.2 L of solution and the proper catalyst amount (Table 1) was suspended in it, in case adjusting pH. Before starting the irradiation of the reaction mixture the system was outgassed at constant CO_2 flow of 15 mL min^{-1} at a pressure of 13 bar with the aim to eliminate air from the reactor head space. Then, in order to saturate water with CO_2 , a static pressure of 7 bar of CO_2 was applied overnight.

Tests were performed, predominantly exploring the effect of reaction time, pH and catalyst mass. The operating parameters of each test are summarized in Table 1.

The amount of hole scavenger (sodium sulphite, 2.0 g) was kept constant, together with the temperature (80°C) and the CO_2 gas pressure (7 bar). These conditions were deeply explored in our previous work and correspond to a good compromise between productivity in gas and liquid phase products [15,16]. Test 7 was carried out at a neutral pH value in order to understand the influence of this parameter on the product distribution and hydrogen productivity.

The results were expressed either as total amount (mol) or as productivity ($\text{mmol/h kg}_{\text{cat}}$, which is equivalent to $\mu\text{mol/h g}_{\text{cat}}$). In the latter case the total amount of product was normalised by catalyst mass and by total irradiation time up to the sampling moment.

3. Results and discussion

Reproducibility of the measurements allowed to define an average error ca. 7% (maximum value 14%).

Blank tests were carried out by irradiating only a water suspension of the photocatalyst for 24 h, pressurizing the reactor with N_2 . We obtained a productivity of $54 \text{ mmol/h kg}_{\text{cat}}$ for H_2 due to water splitting, plus traces of organic compounds. The latter may be ascribed to the decomposition of possibly adsorbed organic species on catalyst surface (e.g. residua of catalyst synthesis) or to the sensitivity of the HPLC instrument. The first reason is unlikely due to the selection of P25 as reference catalyst. The operating conditions were 7 bar of N_2 , 80°C , pH 7 with 0.5 g/L TiO_2 suspension in water

and $1.8 \text{ g/L of } \text{SO}_3^{2-}$. A further blank test without the catalyst under CO_2 pressure did not evidence any product in gas phase and slightly higher concentration of organic products in liquid phase.

Experimental results concerning tests 1–5 with detail on liquid phase products and the concentration of Na_2SO_3 are reported in Figs. 2 and 3, respectively.

From Fig. 2 one may observe that both formic acid and formaldehyde were detected, while only traces of methanol formed. As previously discussed in the introduction section, the mechanism of the CO_2 photoreduction has been previously studied and may lead to a broad spectrum of products depending on photocatalyst formulation and reaction conditions, as a result of many parallel and consecutive reaction steps [6]. A strictly consecutive path were assumed at first (Scheme 1).

According to this scheme, we would expect concentration maxima at increasing reaction time in the order: formic acid, formaldehyde and methanol. Gas phase product should start forming after accumulation of significant amounts of organic products in liquid phase through a photoreforming consecutive step. The higher formation rate of formaldehyde at the beginning of the reaction cannot be explained based on this mechanism.

The present reactions were operated at a basic pH, thus in the presence of dissolved CO_2 and carbonate anions. Chandrasekaran et al. [18] demonstrated that the direct reduction of carbonate to formaldehyde could be achieved, without the formation of formic acid. Compared to that reference, in which a 150 W Xe lamp was used, we obtained a maximum concentration of formaldehyde three orders of magnitude higher, which allowed us to obtain also a detectable amount of methanol, although minor with respect to the other intermediate products.

We therefore interpret our experimental results on the basis of the coexistence of a parallel reaction mechanism, involving in one branch the reduction of molecular carbon dioxide to formic acid, which may further evolve to gas phase products, and in the second branch the reduction of carbonates to give formaldehyde and possibly methanol in a further consecutive step, as shown in Scheme 2.

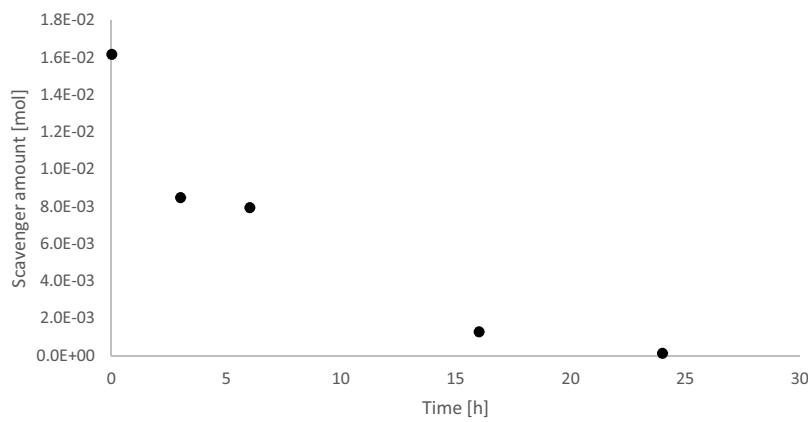
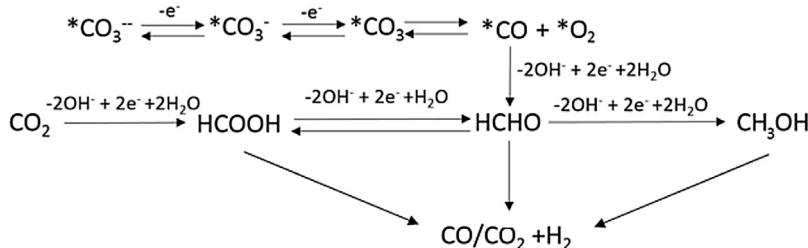


Fig. 3. Amount of scavenger at the end of tests 1–5.



Scheme 2. Parallel pathways for molecular CO_2 and carbonate photoreduction. *Indicate the species adsorbed on the photocatalyst surface.

More in detail, we assumed the existence of consecutive reduction reaction because, due to the high pH of the solution, the presence of hydroxyl anions is not negligible also at the catalyst surface and, according to Ao et al. [19], the back-oxidation reaction may occur.

The photoreduction of CO_2 has negligible rate in the absence of a hole scavenger. Indeed, if the consumption of conduction band electrons is not efficiently accompanied by holes reduction through electron donating species, the reaction is depressed. In this work we selected sodium sulphite as hole scavenger, being an inorganic, not competing species, which demonstrated very active in our previous screening. Fig. 3 reports that the hole scavenger concentration decreased steadily during time and in about 24 h all the Na_2SO_3 was consumed. Indeed, the concentration of scavenger measured in test 1, i.e. after 70 h of reaction, was zero. At the same time, liquid phase products concentration decreased. In particular, formaldehyde was rapidly converted, formic acid slowly decreased its concentration and gas phase products started forming. Gas phase production expressed as moles of hydrogen and carbon monoxide versus time for tests 1–5 are reported in Fig. 4.

Gas phase products were detected only after 16 h of reaction and then steadily increased with reaction time. This observation confirms the consecutive reaction step previously proposed by our group, in particular, the evolution of hydrogen was attributed to the degradation of formic acid (see Scheme 2) because, comparing Figs. 2 and 4, the inflection point of the hydrogen formation curve (maximum formation rate) corresponds to the maximum peak of formic acid concentration. It should be noticed that photoreforming may also occur with formaldehyde, but the main reaction product after the consumption of the inorganic hole scavenger was formic acid in this case. Therefore, when the inorganic hole scavenger is finally consumed, the oxidation of sacrificial organic species starts. The latter reaction is indeed much more efficient than water oxidation. The highest amount of hydrogen was obtained after 70 h reaction time, corresponding to a specific productivity of $57.1 \text{ mmol h}^{-1} \text{ kg}_{\text{cat}}^{-1}$. Specific productivities were calculated

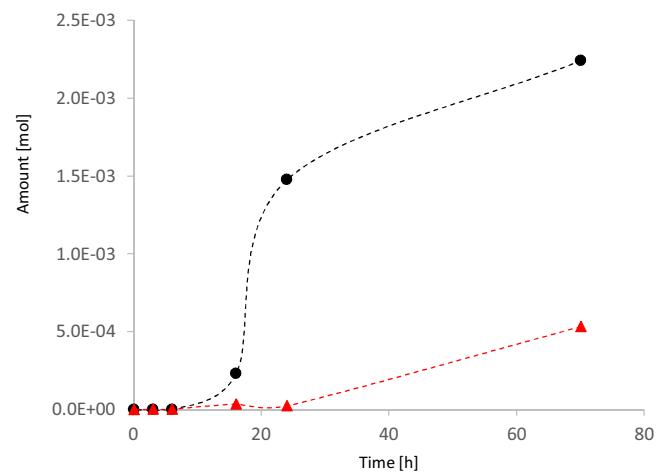
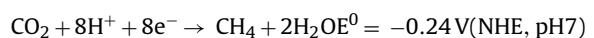
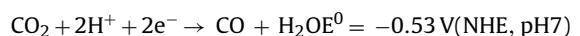


Fig. 4. Gas phase products, i.e. CO (▲) and H_2 (●) amount obtained in tests 1–5.

by dividing the cumulative amount of each species by the catalyst mass and total irradiation time up to the sampling moment (including any induction period). Differently from other works in literature [20,21], no methane was detected in the gas phase. This is reasonable according to literature data on band edge position and potentials of the redox couples involved in the reaction. The reaction involved in the CO and CH_4 generation are the following [22]:



The potential level of the conduction band of TiO_2 P25 is more negative ($E^0 = -0.56 \text{ V}$ vs. NHE, pH 7) [23] therefore both reactions are feasible under UV irradiation. However the formation of CH_4 requires 8 electrons, compared with the 2 electrons of CO forma-

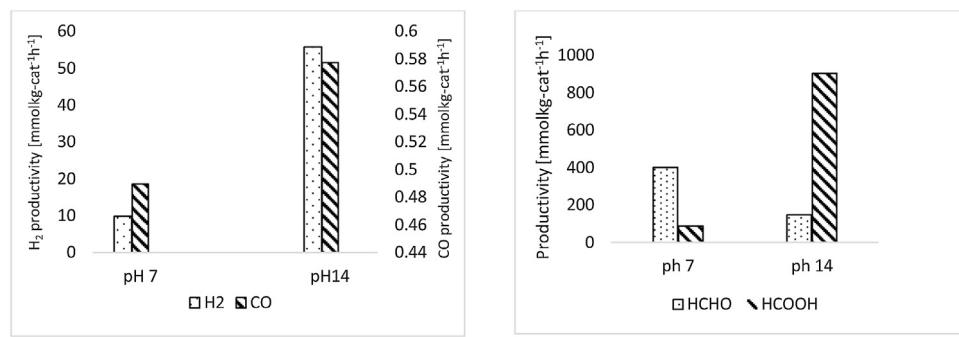


Fig. 5. Productivity of gas (a) and liquid (b) products in function of pH.

Table 2

Experimental results expressed as gaseous and liquid productivity changing catalyst amount.

	Catalyst concentration [g L ⁻¹]	Productivity [mmol h ⁻¹ kg _{cat} ⁻¹]				
		H ₂	CO	HCOOH	HCHO	CH ₃ OH
test 1	0.5	54.24	12.81	58.97	80.94	0
test 2	0.5	102.56	1.69	902.58	145.98	0
test 3	0.5	23.71	3.59	655.63	1411.38	0
test 4	0.5	0.00	0.72	1859.31	16537.13	350.98
test 5	0.5	0.00	0.91	2954.37	12350.14	0
test 6	0.25	98.21	8.85	1784.64	0	0

tion. Therefore the formation of CO is favored in the case of a bare semiconductor as in the present case and was confirmed by literature reports [22,24]. Moreover CO may be the precursor for CH₄ generation following an alternative hydrogenation pathway [25].

Furthermore, CH₄ formation was reported for Au-loaded samples, whereas reduction to formic acid was the only reaction path connected with undoped TiO₂ according to different authors [15,16]. On such basis, we here selected to operate in this work on bare TiO₂, at difference with our previous reports on Au/TiO₂ samples [15,16], to avoid the concomitance of CO₂ photoreduction to methane, which would have introduced a further complication in the reaction mechanism.

A very interesting point is that the photoreforming reaction to gas phase products did not start only after accumulation of organic compounds in liquid phase, but also after exhaustion of the inorganic hole scavenger. Thus, after almost complete conversion of Na₂SO₃ was accomplished, H₂ evolution started. This confirms the hole scavenging role of the organic compounds in liquid phase.

A comparison between the produced amount of hydrogen, carbon monoxide, formaldehyde and formic acid are reported for test 7 and 2, i.e. under the same operating conditions for 24 h but at different initial pH (Fig. 5). For tests at basic pH the measured initial value was pH = 14, ending at 9 after CO₂ saturation and whole testing.

We worked in most tests at basic pH to raise the solubility of CO₂ in the aqueous medium in the form of carbonates and to enhance the formation •OH species [26]. However, the drawback of working at high pH is the conversion of CO₂ into CO₃²⁻ or HCO₃⁻ that are harsher to reduce than CO₂ itself [27]. At pH 14, an increased CO₂ solubility in the liquid phase is obtained in form of carbonate ions, and thus higher gas and liquid phase products concentration was obtained. However, considering the results at neutral pH (test 7), a different product distribution is obtained compared to the one of test 2. In particular, in liquid phase, a higher amount of formaldehyde was detected, while in test 2 higher concentration of formic acid than formaldehyde was obtained after 24 h. This is probably due to the different carbonate concentration, which decrease significantly at neutral pH, making the reaction mechanism depicted in Scheme 1 predominant with respect to Scheme 2.

Moreover, considering Scheme 2, the amount of hydroxyl anions is greatly reduced from pH 14 to pH 7, and thus the back oxidation of formaldehyde to formic acid is inhibited.

Finally, the results concerning the productivity of liquid and gas phase products is reported for test 2 and 6 in Table 2, carried out with different catalyst amounts. The catalyst concentration here adopted was lower than that reported by de los et al. [28,29]. Indeed, they concluded that when the photocatalytic reaction is not fast, employing catalyst concentration below 1 g/L and very good mixing operation (we optimised this point in a previous work), it is always safe to assume that mass transport limitations in the bulk of the fluid are nonexistent.

As for gas phase products distribution, we can attribute the increase of CO concentration and the slight decrease of the H₂ one to a less effective photoreforming activity, due to the lower catalyst amount. This leads to incomplete oxidation of the substrate back to CO₂, leaving a greater amount of CO and limiting slightly the H₂ productivity. Accordingly, formic acid was the only product of reaction in liquid phase.

4. Conclusions

The photoreduction of CO₂ has been explored under unconventional reaction conditions. The increase of operating pressure allowed increasing CO₂ solubility in liquid phase, thus improving the overall performance with respect to literature data. By considering products distribution vs. reaction time, unexpectedly formaldehyde formed independently from formic acid and constituted the major product at the beginning of the reaction. Two parallel pathways were hypothesised for the formation of the aldehyde and the acid, the former active when CO₂ is chemically dissolved as carbonate, the other involving the physical dissolution in molecular form.

Sulphite confirmed its role as inorganic hole scavenger. When it was completely converted, the oxidation of organic compounds accumulating in the reactor started. This allows confirming that gas phase products (CO and H₂) form through a consecutive mechanism by photoreforming of the formaldehyde and formic acid produced by CO₂ photoreduction.

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